Superconducting Properties of Atomic-Disordered Compound $MgCNi_3$

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The effect of radiation-induced disordering in a nuclear reactor (fast neutrons fluence $\Phi = 5 \cdot 10^{19}$ cm^2, $T_{\rm irr} = 340$ K) on resistivity ρ, superconducting transition temperature T_C and upper critical field H_{C_2} of polycrystalline $MgCNi_3$ samples was investigated. It was found that T_C decreases under irradiation from 6.5 to 2.9 K and completely recovers after annealing at 600 °C. Temperature dependences $\rho(T)$ are characteristic of compounds with strong electron-phonon interaction. The dH_{C_2}/dT behaviour testifies to a considerable decrease in density of electronic state at Fermi level $N(E_F)$ in the course of disordering.

Radiation-induced disordering caused by irradiation with high-energy particles is a unique method of investigating the properties of superconducting and normal states of ordered crystals [1, 2]. Even in broad-band metals, such as intermetallic compounds with A15 structure, long-range ordering loss leads to considerable rearrangement of the electronic spectrum, resulting in disappearance of individual features of the electronic structure. Disordering causes decrease in densities at Fermi level $N(E_F)$ and respective noticeable drop of T_C in compounds with high initial $N(E_F)$ (Nb_3Sn or V_3Si), and considerable (from 1.5 to 7 K) rise of T_C in compounds with low $N(E_F)$ and T_C due to growth of $N(E_F)$ (Mo_3Si and Mo_3Ge) [3, 4, 5]. In type HTSC compounds, disordering leads to more significant changes in properties: fast and complete T_C degradation is accompanied with $N(E_F)$ decrease and metal-insulator transition [2]. Thus investigation of response of a system to radiation-induced disordering serves as a kind of a test to reveal the characteristic features of its electron states. It was shown in recent papers [6, 7] that T_C drop from 38 to 5 K observed at MgB_2 under radiation-induced disordering is connected mainly with considerable drop of $N(E_F)$, similar to Nb_3Sn or V_3Si compounds. In our investigation, we concentrated on the effect of disordering on the properties of superconducting compound $MgCNi_3$ ($T_C \sim 8$ K) with perovskite cubic structure of type $SrTiO_3$, unconventional for intermetallides [8]. Our interest in this system was explained by the fact that its ground state is close to ferromagnetic due to the presence of a narrow peak in $N(E)$ located 45 meV below the Fermi level [9]. This allowed us to regard it as a candidate for an unconventional (possibly triplet) superconductivity, similar to Sr_2RuO_4 compound. It is known that in Sr_2RuO_4, as distinct from conventional superconducting compounds (intermetallides), T_C undergoes anomalously strong suppression even under a slight disorder [10]. In $MgCNi_3$, maximum T_C is achieved at excess of carbon content only (nominal composition $MgC_{1.5}Ni_3$), even though, according to neutron diffraction study, the actual composition is closer to $Mg_{0.96}CNi_3$, and excess carbon occupies the region between sample grain boundaries [11].

In the sample preparation, fine powders Mg, C and Ni with purity better than 99.5% were used as starting materials. The mixtures of appropriate composition were pressed into pellets; the pellets were wrapped in Ta foil and enclosed in an evacuated quartz tube, placed in a furnace, heated to 950 °C at a rate of 150 °C/h and kept at this temperature for 5 h, followed by furnace-cooling to room temperature. The highest $T_C = 6.5$ K and the best superconducting transition corresponded to the nominal composition $x = 1.45$ [12]. Samples $0.5 \times 1 \times 5$ mm^3 in size were irradiated with fast neutrons at $T_{\rm irr} = (330 \pm 10)$ K, then annealed during 20 min at temperatures $T_{\rm ann}$ from 100 to 600 °C in step of 100 °C. Resistivity $\rho(T)$ in fields up to 13.6 T was measured using a standard four-probe method.

The initial sample resistivity curve of transition to superconducting state (Fig. 1) is stretched in the direction of higher temperatures, onset is about 8 K. Mean transition temperature is 6.5 K. We defined the superconducting transition temperature T_C as the temperature exhibiting half of the normal-state resistivity. Irradiation leads to T_C drop to 2.9 K, and transition becomes narrower. Annealing at 500 °C almost completely recovers the initial form of dependence $\rho(T)$, while after annealing at 600 °C, transition becomes more abrupt with a higher $T_C = 7.1$ K compared with the initial sample.

Temperature dependences $\rho(T)$ of the initial, irradiated and isochronally annealed $MgCNi_3$ samples (Fig. 2) present curves with saturation, typical of the systems with strong electron-phonon interaction of types Nb_3Sn or V_3Si [3]. A rather large value of residual resistivity $\rho_0 = 0.137$ mOhm· cm (found by ρ extrapolation to $T = 0$) of a sample in the initial state testifies to an insufficient degree of ordering. The absolute value of $\rho(T)$ approximately coincides with the data in [13] and is three times higher than in [8], even though temperatures dependences $\rho(T)$ are practically

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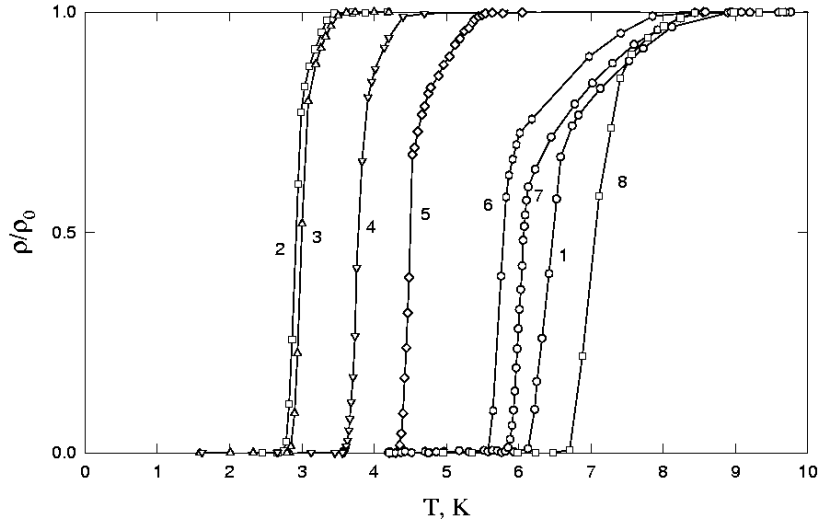

FIG. 1: Temperature dependences of reduced resistivity ρ/ρ_0 of initial $MgCNi_3$ sample (1), sample irradiated under fast neutrons fluence $\Phi = 5 \cdot 10^{19}$ cm^{-2} (2) and sample annealed at T = (100 - 600) °C during 20 min. (3 - 8). Solid lines are drawn across experimental points.

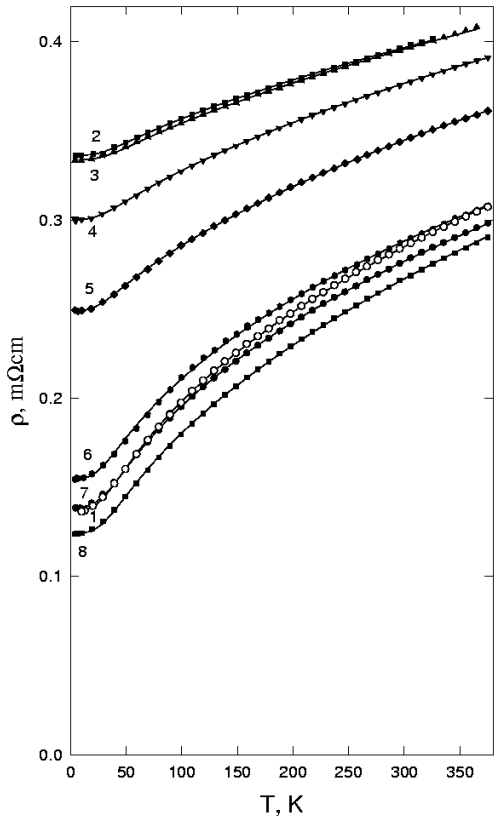

FIG. 2: Temperature dependences of $MgCNi_3$ sample resistivity $\rho(T)$; for designations, see Fig. 1. Solid lines present the calculation using expression (7).

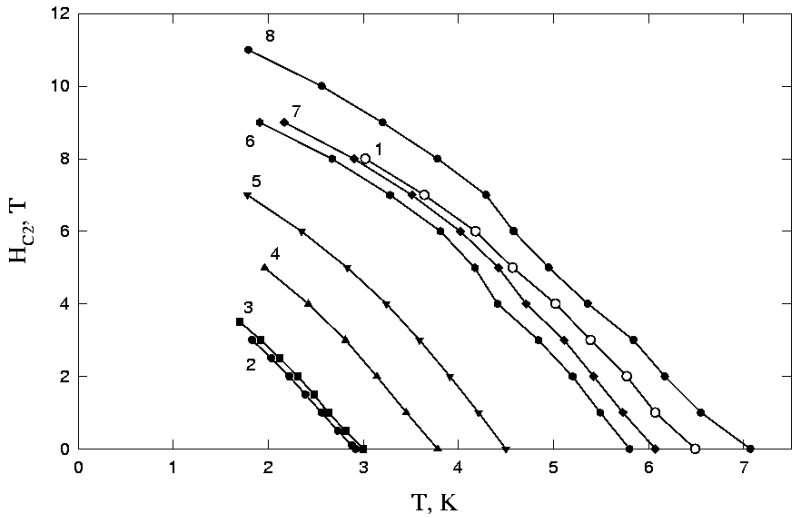

FIG. 3: Temperature dependences of upper critical field H_{C_2} for $MgCNi_3$ sample; for designations, see Fig. 1. Solid lines are drawn across experimental points.

identical in all cases. Evidently, after irradiation and subsequent annealing at 600 °C, further ordering and residual resistivity drop to $\rho_0 = 0.124$ mOhm·cm occur in the sample.

The upper critical field H_{C_2}, as determined from the half-transition temperature (0.5 of the normal-state resistivity), has a form typical of second-order superconductors (Fig. 3), the initial sample value of dH_{C_2}/dT is in good agreement with the data of paper [13]. A relatively weak change in the slope of dH_{C_2}/dT should be noted; a very similar behaviour at disordering was observed for MgB_2 [6]. So, for dirty superconductor

$$(-dH_{C_2}/dT)_{\rm dirty} = (8ek_B/\pi)(1+\lambda)N(E_F)\rho_0, \tag{1}$$

the relatively weak change in dH_{C_2}/dT (Fig. 3) would evidently be compensated by a considerable (about 2.5 times) decrease in $N(E_F)$.

Deviations from the Block-Gr$\acute{}$uneisen law

$$\rho(T) = \rho_0 + \lambda_{\rm tr} F_{\rm BG}(\theta/T), (2) \tag{2}$$

defining linear behaviour of $\rho(T)$ at high T, where θ is Debye temperature, $\lambda_{\rm tr}$ is electron-phonon interaction constant proportional to parameter λ in the McMillan expression for superconducting transition temperature

$$T_C \sim (\omega_{\ln}/1.2)\exp\{-(1+\lambda)/(\lambda-\mu)\}, \quad \mu \sim 0.1, \tag{3}$$

are often described by an empirical expression

$$1/\rho(T) = 1/\rho_{\rm sat} + 1/(\rho_0 + \lambda_{\rm tr} F_{\rm BG}(\theta/T)), \tag{4}$$

so $\rho(T)$ cannot exceed the value of saturation resistivity $\rho_{\rm sat}$, which for type A15 intermetallides is about 0.2 mOhm·cm. Intuitive substantiation of (4) boils down to the fact that electron scattering becomes inefficient when the electron free path $l_{\rm tr}$ becomes shorter than the Fermi wavelength, inversely proportional to wave-vector k_F; therefore, in the expression for conductivity $\sigma \sim (k_F)^2 l_{\rm tr}$, $l_{\rm tr}$ should be substituted by a value close to $(k_F)^{-1}$. The interpolation formula $\sigma \sim (k_F)^2 l_{\rm tr} + k_F$ is equivalent to (4).

Fitting of experimental data on $MgCNi_3$ to expression (4), containing 4 fitting parameters $\rho_{\rm sat}$, ρ_0, $\lambda_{\rm tr}$ and θ, yields good agreement with the close values of $\theta = (140-155)$ K. A similar fitting procedure for $MgCNi_3$ ($T_C \sim 8$ K) carried out in [12] with Einstein, instead of Debye, spectrum, yields the following parameters: Einstein temperature $\theta_E = 206$ K, $\rho_{\rm sat} = 0.574$ mOhm·cm. The obtained value of θ is noticeably lower than that obtained in heat capacity measurements, Debye temperature $\theta_D \sim 235$ K [8]. However, using the value of $\theta = 150$ K and on the assumption of the Debye spectrum, we obtain $\omega_{\ln} = \exp(-1/3)\cdot\theta \sim 105$ K, which is considerably lower than $\omega_{\ln} \sim 480$ K for

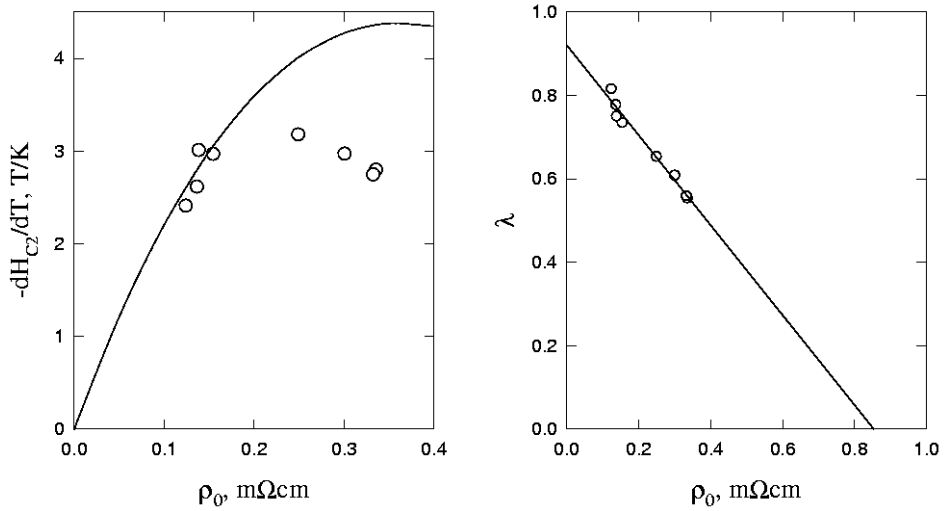

FIG. 4: Upper critical field derivative $-dH_{C_2}/dT$ (left) and electron-phonon interaction constant λ (right) for $MgCNi_3$ sample as a function of residual resistivity ρ_0. Solid lines present the calculation using expressions (8) and (4), respectively.

MgB_2 [14]. Expression (3) yields $\lambda \sim 0.8$, which compares well with the value of $\lambda \sim 1.1$ for MgB_2 [13]. Value λ as a function of ρ_0 (Fig. 4) may be described with a linear dependence

$$\lambda = \lambda_0(1 - (\rho_0/R)), \tag{5}$$

where $\lambda_0 = 0.92$, and $R = 0.85$ mOhm·cm.

The relatively large value of λ (and hence, $\lambda_{\rm tr}$) is generally in an agreement with significant nonlinearity of $\rho(T)$ characteristic of compounds with strong electron-phonon interaction. However, fitting parameter $\rho_{\rm sat}$, varies significantly from 0.85 mOhm·cm for the initial sample to 0.5 mOhm·cm for the irradiated sample, which agrees poorly with the meaning of value $\rho_{\rm sat} \sim (kF)^{-1}$, which must be constant in case of a broad-band metal.

The origin of $\rho(T)$ "saturation" for systems with strong electron-phonon interaction were analyzed in terms of the mean field theory in [15], where it was shown that (in case of a relatively weak coupling which does not lead to formation of a pseudogap) scattering rate is proportional not to the value of ions r.m.s. displacement $\langle u^2 \rangle$, but rather to $(\langle u^2 \rangle)^{0.5}$, and so, in this case, instead of (2), we have

$$\rho(T) = \{(\rho_0)^2 + \lambda_{\rm tr} F_{\rm BG}(\theta/T)\}^{0.5}, \tag{6}$$

which results in type $\rho(T) \sim T^{0.5}$ behaviour at high T. However, use of (6) fails to yield a satisfactory data description. The probable reason is that value $\lambda_{\rm tr}$, in its turn, also depends on disordering (is characterized by a sum of static and thermal displacements), i.e., on $\rho(T)$; the same reason causes decrease in λ with increase in ρ_0 (Fig. 4). Considering $\lambda_{\rm tr}$ being in dependence on $\rho(T)$, similar to that of λ on ρ_0 in (4), expression (6) is transformed into an equation

$$\rho(T) = \{(\rho_0)^2 + \lambda_{\rm tr0}(1 - \rho(T)/R_{\rm tr})(F_{\rm BG}(\theta/T))\}^{0.5}, \tag{7}$$

which, when solved for $\rho(T)$, yields the required expression, also containing four fitting parameters $R_{\rm tr}$, ρ_0, $\lambda_{\rm tr}$ and θ. Expression (7) describes data with the same accuracy as expression (4), with similar values of θ, but with almost equal fitting parameters $R_{\rm tr}$ varying within (0.75 - 0.88) mOhm·cm. Such a good agreement between the values of R in (5) and $R_{\rm tr}$ in (7) does not look casual.

In conclusion, let us consider the probable causes of superconductivity degradation in $MgCNi_3$ under disordering. Loss of long-range order must lead to smearing of the fine structure of electron densities of state; at that, function $N(E)$ smoothes out, but without becoming zero. For superconductors with electron-phonon interaction, $\lambda \sim N(E_F)$, therefore T_C should never go down exactly to zero; the latter requirement is evidently satisfied for the majority of compounds which may be related to broad-band intermetallides. A qualitatively different behaviour is observed in HTSC compounds: in all cases superconductivity is completely depressed at a mush higher rate than in intermetallides, probably due to non electron-phonon mechanisms of superconductivity as well as to a proximity to metal-insulator transition [16].

Value λ calculated by expression (3) decreases 1.5 times at $MgCNi_3$ under irradiation (Fig. 4), while the above value of $N(E_F)$ estimated using expression (1) decreases almost 2.5 times. Probably, such discrepancy in change of λ and $(-dHC_2/dT)$, as it was similarly supposed for, e.g., MgB_2 [6], may be due to the fact that the dirty limit of $l_{\rm tr} \ll \xi$ is not reached in the given region. Coherent length ξ may be estimated from the relation

$$\xi^2 = \Phi_0/\{2\pi(-0.69 dH_{C_2}/dT)T_C\},$$

which yields $\xi = 55$ and 75 $\mathring{A}$ for the initial and the irradiated samples, respectively. Free path $l_{\rm tr}$ may be estimated from an conventional expression used for conductivity

$$(\rho_0)^{-1} = (3\pi^2)^{-1/3}(e^2/\hbar)n^{2/3}l_{\rm tr},$$

which yields $l_{\rm tr} \sim 20$ $\mathring{A}$ for $\rho_0 = 0.137$ mOhm·cm (initial sample) and $l_{\rm tr} \sim 8$ $\mathring{A}$ for $\rho_0 = 0.337$ mOhm·cm (irradiated sample). These relations of $l_{\rm tr}$ and ξ are definitely closer to the dirty limit. Further, expression (1) allows us to estimate $(-dH_{C_2}/dT)$ using the experimental values of γ and ρ_0 or those obtained from band calculations $N(E_F)$. According to band calculations [9, 17, 18], $N(E_F) \sim 2.5$ (eV·spin·cell)$^{-1} = 2.8\cdot10^{47}$ (J·m^3)$^{-1}$, using $\lambda \sim 0.8$, $\rho_0 \sim 0.1$ mOhm·cm, we obtain $(-dH_{C_2}/dT) \sim 3$ T/K, which is quite commensurate with the experimental value $(-dH_{C_2}/dT) \sim 2.5$ T/K. Thus there are probably no reasons to doubt the dirty limit applicability in the given case. Assuming $\lambda \sim N(E_F)$, using (1) and (5), we obtain the dependence

$$(-dH_{C_2}/dT)_{\rm dirty} \sim \lambda(1+\lambda)\rho_0 = \lambda_0\{1-(\rho_0/R)\}(1+\lambda_0\{1-(\rho_0/R)\})\rho_0, \quad (8)$$

shown as a solid line in Fig. 4. The causes of noticeable deviations at $\rho_0 > 0.25$ mOhm·cm are unclear, it should be noted only that very similar changes in dH_{C_2}/dT at radiation-induced disordering were observed for MgB_2 [14]. Nevertheless, for $MgCNi_3$, the response to disordering is similar to that observed for conventional systems (intermetallides) with strong electron-phonon interaction.

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